PREPARATION AND PROPERTIES OF RARE-EARTH COMPOUNDS

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Prepared for:

Advanced Research Projects Agency

31 December 1972

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Final Technical Report
(3 June 1972 to 31 December 1972)

December 31, 1972

by

V. E. Wood, A. E. Austin, and K. C. Brog

Sponsored By

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Under

ARPA Order No. 1588
PRON: W2-71-UX316-D1-DZ
Contract No. DAAH01-70-C-1076

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Monitored by: ARPA Support Office
U. S. Army Missile Command (AMSMI-RND)
Redstone Arsenal, Alabama

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505 King Avenue
Columbus, Ohio 43201

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author) Battelle-Columbus Laboratories 505 King Avenue Columbus, Ohio 43201	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3 REPORT TITLE

PREPARATION AND PROPERTIES OF RARE-EARTH COMPOUNDS

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Technical Report (3 June 1972 to 31 December 1972)

5 AUTHOR(S) (First name, middle initial, last name)

Van E. Wood, Alfred E. Austin, and Kenneth C. Brog

6 REPORT DATE December 31, 1972	7a. TOTAL NO OF PAGES 41	7b. NO OF REFS
8a. CONTRACT OR GRANT NO DAAH01-70-C-1076 b. PROJECT NO c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) Battelle Project # G-0550 9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	

10 DISTRIBUTION STATEMENT

Distribution of this Document is Unlimited

11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY Advanced Research Projects Agency Arlington, Virginia 22209

13 ABSTRACT

The principal portion of the present report consists of a survey of proposed applications of materials having both magnetic and ferroelectric ordering and/or displaying magnetoelectric coupling effects, together with an assessment of the extent to which any of these applications is feasible using presently known materials. Novel, and in some ways superior, devices of the "signal-processing" type (such as amplitude or phase modulators) operating at frequencies from microwave to visible are possible in principle, although considerable further experimental work is necessary before it can even be shown that effective specific devices can be designed. Magnetoelectric memory devices do not at present seem very feasible. A brief survey of other work on this program is also included.

DD FORM 1 NOV 68 1473

UNCLASSIFIED

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Magnetoferroelectric Materials						
Rare-earth chalcogenides						
Rare-earth ferrites						
Bismuth ferrite						
Microwave materials						
Optical materials						

SUMMARY

The principal portion of the present report consists of a survey of proposed applications of materials having both magnetic and ferroelectric ordering and/or displaying magnetoelectric coupling effects, together with an assessment of the extent to which any of these applications is feasible using presently known materials. Novel, and in some ways superior, devices of the "signal-processing" type (such as amplitude or phase modulators) operating at frequencies from microwave to visible are possible in principle, although considerable further experimental work is necessary before it can even be shown that effective specific devices can be designed. Magnetcelectric memory devices do not at present seem very feasible. A brief survey of other work on this program is also included.

GENERAL DISCUSSION

This is the final report on a program on development of device potential of rare-earth compounds. The principal task of the final six months of the program has been preparation of a survey of possible applications of magnetoelectric materials (many of which contain rare-earths) and an assessment of the potential for early realization of these applications on the basis of what is presently known of magnetoelectrics. This survey follows these general remarks. The bulk of the experimental work on the program has been discussed in previous reports; we provide only a very brief summary, emphasizing the most recent developments, here.

The two principal areas of experimental work have been 1) development of materials showing both ferroelectric and ferromagnetic order in some useful temperature range (Table III of the accompanying survey indicates there are possible applications of magnetoferroelectrics for which a net magnetic moment is required as well as ones for which antiferromagnetism is sufficient) and 2) investigation of the nature of the interaction among the rare earths in such compounds as the chalcogenides, which are of potential technological interest owing to their semiconductor-to-metal transitions. In the former area, we believe our principal accomplishment was in substantiating that appreciable weak ferromagnetism could be introduced into the otherwise antiferromagnetic and ferroelectric rhombohedral compound $BiFeO_3$ by partial substitution of the bismuth by a rare earth (in our case, Nd). While the nature of the interaction responsible for the weak ferromagnetism is still not entirely clear, a plausible discussion based on the structural changes known to occur on solid solution of a rare earth can be given, and the possibility that the effect is not an intrinsic property of the rhombohedral-phase solid solution is very remote. A study

of piezoelectric properties of these materials was consistent with ferroelectricity being retained in the solid solutions. Earlier work on rare-earth manganite-chromite and manganite-ferrite solid solutions is described in our previous reports and publications.

In the area of the rare-earth chalcogenides, the principal work was a study of nuclear magnetic resonance and magnetic susceptibility in SmSe and $SmSe_{1-x}S_x$ solid solutions. Large negative shifts were observed in the Se^{77} magnetic resonance. These shifts, which were strongly dependent on temperature and varied linearly with sulfur concentration, were found to be correlated with the expectation value of the rare-earth spin. From these data, it is possible to obtain the value of the transferred hyperfine field at the Se site and the approximate dependence of this quantity on the lattice spacing. This provides information on inter-samarium interactions through the excited states.

In addition to those areas already mentioned, work was carried out on a number of related problems, but either was concluded because it appeared less relevant to possible applications or has still not been analyzed. Among these other areas of investigation were: interactions among rare-earth dopant ions in fluorides, preparation and electrical properties of rare-earth pnictides, cathodoluminescence in rare-earth chalcogenides, second-harmonic generation in rare-earth manganites and chromites, and infrared absorption in several of the materials prepared for other purposes. Some details can be found in our previous reports.

The following publications have resulted from the present program:

1. C. M. Verber, D. R. Grieser and Wm. H. Jones, Jr., "Cooperative and Sequential Excitation of Red Fluorescence of Ho^{3+} in CaF_2", J. Appl. Phys. 42, 2767 (1971).

2. A. E. Austin, J. F. Miller and V. E. Wood, "Solid Solutions of $YbMnO_3$-$YbCrO_3$ and $YbMnO_3$-$YbFeO_3$", Proc. 9th Rare-Earth Research Conference (Blacksburg, Va., 1971) p. 786 (National Tech. Info. Service, Springfield, Va. 22151, report CONF-711001).

3. Van E. Wood, "Indirect Exchange in EuB_6", Phys. Letters 37A, 357 (1971).

4. Van E. Wood, A. E. Austin, E. W. Collings and K. C. Brog, "Magnetic Properties of Heavy-Rare-Earth Orthomanganites", J. Phys. Chem. Solids (to be published, 1973).

5. Van E. Wood and A. E. Austin, "Weak Ferromagnetism in $BiFeO_3$-$NdFeO_3$ Solid Solutions", Proc. 18th Annual Conf. on Magnetism and Magnetic Materials (AIP Conference Procs., to be published, 1973).

6. Van E. Wood, A. E. Austin and R. Smith, "Magnetic and Structural Properties of Heavy-Rare-Earth Ferrite-Manganite Solid Solutions", Proc. 10th Rare-Earth Research Conf. (to be published, 1973).

7. K. C. Brog and R. P. Kenan, "Exchange Induced Hyperfine Fields in the Samarium Monochalcogenides" (submitted for publication, Phys. Rev. B).

Several additional papers are planned.

POTENTIAL APPLICATIONS OF MAGNETOELECTRIC MATERIALS

Introduction

The purpose of this report is to attempt a realistic appraisal of the potential for application of magnetoelectric materials. Both those materials developed in the present program and other materials will be considered. The discussion will be limited, however, to what is known or can be legitimately assumed about materials already prepared and their close relatives, and the possibility of any dramatically superior materials being discovered will be discounted. By "magnetoelectric materials", (abbreviated "ME") we mean all those materials which in some temperature range either

1) exhibit a magnetoelectric effect in an applied electric or magnetic field, or

2) possess both magnetic and ferroelectric ordering.*

It has been pointed out many times by numerous authors that both these effects could lead to certainly unique and possibly useful devices were the effects

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* We repeat here for convenience our definitions[1] of the more important terms met with in this area. Ferroelectric materials which possess some sort of magnetic ordering in the temperature range in which there exists a spontaneous polarization are called magnetoferroelectrics. If there is any kind of net spontaneous magnetic moment (that is, if the order is not purely antiferromagnetic) the material is called ferromagnetoferroelectric. As it happens, all known examples of these are weak ferromagnets; that is, the order is nearly antiferromagnetic, but a slight canting of the spins leads to a net moment. These materials and other magnetically ordered materials may (or may not, depending on the magnetic point group symmetry[2]) exhibit "the" magnetoelectric effect, which is a dependence of the dielectric polarization on an applied magnetic field and a dependence of the magnetization on an applied electric field. Ordinarily we refer to the "linear" effect (bilinear, if one is talking about the free energy; see Table I) in which the additional polarization or magnetization is proportional to the strength of the applied field; non-linear effects depending on particularly strong applied fields, simultaneous application of electric and magnetic fields, or application of stress, are also possible (see Table I). Examples of materials showing most of the effects discussed in this paragraph are given in Table II.

sufficiently strong, present in a useful temperature range, and present in materials with other desirable characteristics (e.g., optical transparency). This has not proved to be the case so far, although there do not seem to be any fundamental reasons much better materials might not occur. In this report we try to assess whether there are any promising areas for application without counting on such superior ME's being found.

There are several factors which make the preparation of a report of this type rather difficult.

1) Even in the most thoroughly investigated ME's, not all the relevant parameters for device operation have been measured. In some cases, reasonable estimates can be made, but these verge all too easily into guesses that cannot be substantiated.

2) As we will discuss below, many of the most attractive opportunities for applications of ME devices lie in the regions of millimeter and sub-millimeter wavelengths. There are relatively few devices operating in these regions at present, but since interest in these regions is growing rapidly, it can be anticipated that this situation will change over the next few years. A comparative analysis of ME vs. "other" devices is largely precluded by not knowing what "other" will be.

3) There are very few classes of materials (the boracites may be an exception) in which sufficient materials preparation research has been carried out that one can tell what the optimum parameters may be. This is particularly so in the areas of reducing electrical conductivity, improving dielectric, magnetic, or magnetoelectric properties by solid solution, improving optical quality, and obtaining larger crystals. Thus limiting ourselves to those extrapolations that have some basis in experiment may sometimes be too stringent a policy.

So although a critical comparative analysis cannot presently be made, one may at least point out where the possibilities and, within the ground rules already discussed, impossibilities lie.

It is of course first necessary to make some sort of general critical-parameter study to show that effects that are more than marginally observable do occur. Such an analysis has been made, but placing it next would tend to get us ahead of the story. So this discussion is deferred until near the end of the report. This introduction is followed by a short discussion of comparative materials selection, a description of our methods of classifying ME devices, and a short list of types of ME materials of interest. Then, following the critical-parameter analysis, we discuss what appear to us to be the most promising areas for near-term further development and point out those areas in which further work would be particularly desirable. Finally, as an appendix, we list all the ME device concepts we have been able to find in the literature or think up ourselves, together with some comments on overall feasibility and difficulty in reducing to practice.

Bases for Materials Selection

The device designer is frequently faced with a choice among several physical effects for the accomplishment of some desired device function, and with a choice among many materials showing a given effect. If he attempts to rationalize his choice, he will often do so on the basis of a figure of merit (perhaps several) indicating the relative effectiveness of the phenomenon and material under consideration in performing the desired function. Such figures of merit are commonly chosen to be dimensionless and are defined such that "big" means "good". Generally speaking, the "function" of any of the devices considered here is the modification (change of amplitude, frequency, phase, polarization,

etc.) of an electromagnetic, acoustic, or hybrid (e.g., magnetoelastic) wave. For some devices, specification of a principal figure of merit is straightforward.[3] Thus for an isolator, the natural figure of merit is the ratio of reverse to forward attenuation; for a Faraday (plane-polarization) rotator, it is the angle of rotation per unit length divided by the average attenuation in this length; for a phase shifter it is the phase shift per unit average attenuation. For switching and memory devices, specification of a figure of merit is not as simple, but a useful figure for the specific case of magnetooptical memories has recently been developed by Cohen and Mezrich.[4]

Even in the simpler cases, there is a certain amount of arbitrariness in the definition of a figure of merit which is hard to justify on grounds other than simplicity. For instance, if there is a threshold below which power transmitted in the reverse direction through an isolator will not be detected, an increase in reverse attenuation beyond that necessary to reduce the power below this level is of no value and ought not be counted. It should also be borne in mind that there is almost always some time constant—switching or response time—requirement which the material must also meet. And there are many other technological factors that must be considered, such as temperature stability or fabricability, for instance, to say nothing of important additional factors such as familiarity, availability, and cost. Still, the figures of merit provides the si t criterion for materials comparison and we use it where possible. Because of the paucity of experimental data, there are few cases where complete calculations can be carried out, but quantitative discussions of the effects of magnetoelectric and other parameters on the figure of merit can sometimes be given.

Classification of Possible ME Devices

Any ME device may be specified in a fairly general, if somewhat abstract, way by giving

1) its function,
2) its operating range,
3) the magnetoelectric effect used, and
4) any other required characteristics.

Some types of functions of interest have been mentioned in the last paragraph. More specific operations are given in Table III, which is organized predominantly by function. Under the general term "switches" we may include proposed memory devices, which of course just amount to switches with non-destructive sensors of their polarity.

By "operating range", we mean predominantly frequency range of operation, but also mean to include temperature requirements, voltage and power requirements and limitations, etc., as appropriate.

There are a number of ways one can classify devices by the ME effect used. One way is simply to identify the term or terms in the expansion of the free energy in powers of the applied fields important to the device operation. Such an expansion is given in Table I (after Schmid[5]). This is useful for reminding oneself of the effects which may occur, but is a little complicated for our purposes, and does not too easily distinguish effects based on the presence of spontaneous magnetization or polarization from induced effects. So we adopt the following simple scheme:

a) Devices requiring presence of both spontaneous polarization P_{sp} and spontaneous magnetization M_{sp}, but not requiring any interaction between them. (This doesn't seem to be a very promising area.)

TABLE I

Possible expansion (through third-order terms) of the free energy of a solid in external electric (E), magnetic (H), and stress (T) fields together with the phenomena corresponding to each term and the names given to the expansion coefficients. Summation over repeated indexes to be assumed. Expansion coefficients taken to be independent of applied fields. Some formal difficulties exist when E and H (rather than, say, E and B) are taken as the expansion parameters. These are discussed by O'Dell, Electrodynamics of Magnetoelectric Media (North-Holland, 1970), pp. 21-27.

(After Schmid, Réunion Française de Ferro-electricité, Orleans, 1972)

$G = G_o -$	Corresponding Phenomena	Coefficient
$K_i E_i +$	Ferroelectricity (pyroelectricity)	Spontaneous polarization
$\chi_i H_i +$	Ferromagnetism (pyromagnetism)	Spontaneous magnetization
$s_{ij} T_{ij} +$	Ferroelasticity	Spontaneous deformation
$\frac{1}{2} K_{ik} E_i E_k +$	Induced polarization, Brillouin, Raman, Rayleigh scattering	Electric susceptibility
$\frac{1}{2} \chi_{ik} H_i H_k +$	Induced magnetization	Magnetic susceptibility
$\frac{1}{2} s_{ijkl} T_{ij} T_{kl} +$	Elasticity (harmonic approximation)	Elastic compliance
$\gamma_{ik} E_i H_k +$	Magnetoelectric effect	Magnetoelectric susceptibility
$d_{ijk} T_{ij} E_k +$	Piezoelectricity	Piezoelectric coefficient
$g_{ijk} T_{ij} H_k +$	Piezomagnetism	Piezomagnetic coefficient
$\frac{1}{6} K_{ijk} E_i E_j E_k +$	Pockels effect, non-linear optical effects	Non-linear electric susceptibility
$\frac{1}{6} \chi_{ijk} H_i H_j H_k +$	Magnetooptical effects, non-linear optical effects	Non-linear magnetic susceptibility
$\frac{1}{6} s_{ijklmn} T_{ij} T_{kl} T_{mn} +$		"Third-order" elastic constants
$\frac{1}{2} \gamma_{ijk} H_i E_j E_k +$	Induced magnetoelectric effect*	First non-linear magnetoelectric susceptibility
$\frac{1}{2} \gamma_{ijkl} T_{ij} E_k E_l +$	Induced piezoelectric effect	
$\frac{1}{2} \beta_{ijk} E_i H_j H_k +$	Induced magnetoelectric effect	Second non-linear magnetoelectric susceptibility
$\frac{1}{2} \beta_{ijkl} T_{ij} H_k H_l +$	Induced piezomagnetic effect	
$\frac{1}{2} s'_{ijklm} T_{ij} T_{kl} E_m +$		
$\frac{1}{2} s''_{ijklm} T_{ij} T_{kl} H_m +$		
$\pi_{ijkl} T_{ij} E_k H_l + \ldots.$	Piezomagnetoelectricity	Piezomagnetoelectric coefficient

b) Devices requiring interaction between P_{sp} and M_{sp}. Such an interaction might come about through the magnetoelectric tensor, but might also occur via magneto- or electro-striction or other higher-order effects. One might also include here interaction between the polarization and the sublattice magnetization in antiferromagnets. It may be well to point out here that such interaction effects may be expected to be largest near the ferroelectric Curie temperature when that temperature is below the magnetic ordering temperature. This situation is seldom met with, though.

c) Devices based on the interaction between electric and magnetic properties brought about by the non-zero components of the magnetoelectric tensor, whether or not there is a P_{sp} or M_{sp}. (There is some overlap between this category and the previous one.)

d) Devices using ferroelectricity simply to get a high dielectric constant, these devices being more or less conventional "magnetooptical" ones otherwise. (No converse devices - utilizing ferrimagnetism just to get a large magnetic permeability in a ferroelectric - have been suggested, and indeed it is difficult to see what the use of any such thing might be.)

e) Devices based on higher-order ME effects.

f) Devices in which ME effects are not used at all. These are not listed in Table III, but the likelihood that some of the materials studied so far mainly for their magnetoelectric interest will be found to have other useful attributes should not be underestimated. Among the types of applications that might be mentioned are electrooptic or magnetooptic modulators (for instance, iron iodine boracite appears to have electrooptic coefficients[6] comparable to those found in $LiNbO_3$), piezoelectric transducers, pyroelectric detectors, magnetic or ferroelectric semiconductors (both of which might show interesting

negative differential resistance,[7,8] although this has never been demonstrated), high-electric-field switches,[9] and so forth. Many of the materials so far investigated are of the type in which the ferroelectric transition is accompanied by, or even induced by, a spontaneous deformation which is divertible (can be switched between two (or more) different states by an applied stress). These so-called ferroelastic properties (see Table I) may eventually be exploited in devices.

The "other required characteristics" mentioned above (item 4) include such things as preparation in single-crystal form, optical transparency, semiconductivity, etc. Such things are mentioned in the column headed "Comments" in Table III.

Some Types of ME Materials

We present here in tabular form (Table II) a few classes of materials which have been found to have interesting ME properties. This table is based in part on the recent compilations of Schmid,[5] Hornreich,[10] and Bertaut.[11] It should be understood that not all materials in a given class may show the effects described. Moreover, the list, albeit generic, is not complete. In particular, all materials which show the effects of interest only at extremely low temperatures (say less than 20 K) have been excluded, although some of them are of considerable fundamental importance. Also those materials in which the existence of the effects seems to us highly conjectural have been left out. Finally, many new ME materials have been reported in the past year. It has not been possible for us to search thoroughly the very recent literature, though.

TABLE II. SOME TYPICAL CLASSES OF ME COMPOUNDS

Class of Materials	Representatives Selected	Magnetic Ordering*	Electric Ordering*	Magnetoelectric Effects	Comments	Refs.
Transition-metal boracites	$Ni_3B_7O_{13}I$	WFM	FE	measured, magnetic-moment coupling to polarization also demonstrated $\alpha_{max} \sim 5 \times 10^{-4}$ (Gaussian units)	1) Good sized single crystals have been grown 2) Optical transmission is visible fairly good, and crystals hard and polish well. Thus numerous optical experiments have been done 3) Low temperatures (<64 K) required for observation of effects 4) Electric coercive field very high	6,12
Bismuth-rare-earth ferrites (or more generally, Bi-based perovskite-like ferrites)	$Bi_{.9}Nd_{.1}FeO_3$	WFM	FE	predicted by symmetry, not measured	1) Numerous other combinations of $BiFeO_3$ with other perovskite-like compounds have been studied. Weak ferromagnetism in the FE rhombohedral $BiFeO_3$ phase and ferroelectricity in WFM other phases are claimed in some cases. These claims need verification. 2) Growth of crystals rather difficult. FE hysteresis loops actually demonstrated only on pure $BiFeO_3$, which appears to be AFM. 3) Effects occur at room temperature. Magnetism disappears at ~ 350-400 C in $BiFeO_3$; at 130 C in ferrotitanate.	13-16
	$BiFeO_3$	AFM	FE	"		
	$Bi_9Ti_3Fe_5O_{27}$	WFM	FE	recently observed;[16] needs confirmation		

Class of Materials	Representatives Selected	Magnetic Ordering*	Electric Ordering*	Magnetoelectric Effects	Comments	Refs.
					4) Conductivity appears moderately high. Can be reduced by solid solution, oxygen stoichiometry control 5) Electric coercive field high; magnetization somewhat small.	
Lead-based perovskite ferrites and manganites	$PbFe_{2/3}W_{1/3}O_3$	AFM	FE	See comment 4	1) Many compounds and solid solutions of these types have been prepared, and there is much conflicting data about their electric and magnetic properties. This is slowly being straightened out as homogeneous single crystals are prepared. In some cases, not all the d-ions may order magnetically 2) In all materials of this type found to date, at least one of the transitions to ordered state takes place below room temperature 3) Ferroelectric phase transitions tend to be diffuse. Dielectric constants can be very high (apparently up to $\sim 10^4$ at low frequencies). Some compounds tend to have high conductivity. 4) Magnetoelectric coupling has been inferred by indirect means in some related materials;[19] further confirmation would be desirable.	17-19
	$PbFe_{.5}Ta_{.5}O_3$	AFM or WFM	FE	"		

Class of Materials	Representatives Selected	Magnetic Ordering*	Electric Ordering*	Magnetoelectric Effects	Comments	Refs.
Barium-3d fluorides	$BaCoF_4$	AFM	FE	See comment (1)	1) Al'shin et al[21] claim observation of ME effect in $BaCoF_4$ at room temperature. This requires magnetic ordering at that temperature, which seems to be in conflict with neutron diffraction measurements 2) Large, stable, transparent crystals of good optical quality can be obtained 3) Materials FE at room temperature, WFM below ~ 50-120 K 4) Dielectric constants not large, ~ 10-20.	20,21
Heavy-rare-earth manganites	$YbMnO_3$ (hexagonal form)	AFM (some WFM below RE ordering temperature, ~ 10 K)	FE	predicted by symmetry, not measured	1) Magnetic ordering temperatures somewhat low (~ 80-90 K); FE at room temperature 2) Dielectric constants not large, ~ 20-30 3) Antiferromagnetic resonance and some optical properties of single-crystal platelets studied. Transmits in near infrared.	1,22, 23
"Olivines"	$LiFePO_4$	AFM	none	measured, α_{max} ~ 13×10^{-4}	1) Low magnetic ordering temperatures, ~ 50 K.	10, 24
Cr_2O_3	Cr_2O_3	AFM	none	measured, α_{max} ~ 1.7×10^{-4} at 250 K, slight residual effect at RT	1) The original magnetoelectric material, subject of many studies. Small crystals readily prepared; magnetoelectric effect also observable in powder samples.	25,26

Class of Materials	Representatives Selected	Magnetic Ordering*	Electric Ordering*	Magnetoelectric Effects	Comments	Refs.
$Ga_{2-x}Fe_xO_3$	$Ga_{.85}Fe_{1.15}O_3$	FIM, probably	none	measured, $\alpha_{max} \sim 1.7 \times 10^{-4}$ at 200 K, small effect remaining at RT	1) Nature of magnetic ordering for various x ($.6 \leq x \leq 1.3$ for single-phase compounds) still not entirely clear. Ferromagnetic resonance observed in single crystals, see discussion in Table III.	25, 27
Iron garnets and orthoferrites	$Y_3Fe_5O_{12}$	FIM	none	linear ME effect forbidden by symmetry, quadratic effect (in strong applied electric field) measured at RT	1) Included as examples of materials showing higher-order effects.	11,28
	$YbFeO_3$	FIM	none	"		

* Notation: AFM - antiferromagnetic
WFM - weakly ferromagnetic
FIM - (conventionally) ferrimagnetic (antiparallel alignment of sublattices of unequal spin magnitudes)
FE - ferroelectric

Critical Parameters for Device Applications

The essential factors in utilization of magnetoferroelectrics are principally those of importance in ferrimagnets and ferroelectrics separately. These are:

1) Magnetization and reversing magnetic field
2) Polarization and reversing electric field
3) Optical birefringence (natural and induced) and absorption
4) Resonance frequencies of the spin system and their dependence on the applied magnetic field

In addition, the magnitude of the magnetoelectric coefficients and the size of the effective fields they lead to will be of importance in those applications depending on this effect. Application in devices involves either detection of a polarization or magnetization state or dynamic interaction with fields. The major area of interest for static states is that of data storage (memories) while that for dynamic interaction is control of microwaves, particularly millimeter to submillimeter waves. The analysis of critical parameters has been done with viewpoint of possible utilization in these fields.

Memory Requirements

There have been several recent reviews[29,30] on memory systems which have emphasized the hierarchy of the systems with trade-offs among access time, capacity and cost per bit. Typical requirements for fast-access memories for cores are a density of 2×10^5 to 2×10^6 bits/cm^2 with access time of 10^{-6} secs. These values are used in the following two sections.

Magnetization

The sensing of the magnetic state of a bit, i.e., its direction of magnetization, involves the detection of its magnetic flux where φ = induction x Area $\leq \pi^2 d^2 M_s$ (gaussian units), d = bit diameter, and M_s is magnetization per unit volume. An optimistic estimate of minimum detectable flux[31] is 2×10^{-5} maxwells (2×10^{-13} webers) while present devices require an order of magnitude greater. For an area of 5×10^{-6} cm^2, an M_s of 0.3 emu/cm^3 or an induction of 4 gauss is required. The weakly ferromagnetic orthoferrites for detectable domains of this size, 25μ diameter, have M_s values of around 3.6 emu/cm^3 or inductions of 45 gauss while ferrimagnetic garnets with much greater M_s have inductions of 200 gauss for smaller domains of 6μ diameter. Typical bits, 5×10^{-6} cm^2 area, of γ-Fe_2O_3 may have inductions up to 350 gauss. The known magnetoferroelectrics have very weak ferromagnetism. Our data on $Bi_{.9}Nd_{.1}FeO_3$ gave M_s values of 0.14 to 0.45 emu/cm^3 which is just about the estimated minimum detectable value for bits of 5×10^{-6} cm^2. Any increase in bit density, which is desirable, would require higher magnetizations. This could probably be achieved by partial substitution of Al, Ga, or Cr for Fe. No magnetization data are available for nickel-iodine boracite, $Ni_3B_7O_{13}I$. However, the value of M_s is expected to be comparably low, since its transition is from an antiferromagnetic state to a weak ferromagnetic state. For $Ni_3B_7O_{13}Br$ below the Neel temperature of 40 K the magnetization is of order 10^{-2} emu/cm^3.

Polarization

The use of ferroelectrics for digital data storage requires both storage of the charge from polarization and the detection of its sign and magnitude. According to recent reviews[30,32] the characteristics of ferroelectrics are not

nearly as good as magnetic materials for digital data storage and retrival. Leakage limits use for long time storage, and the electrical detection of charge involves some dissipation with resultant reduction on each access. The digital bit size is limited by the minimum stable domain. In sandwiches of thin ferroelectrics/photoconductors, the switching and detection of charge has been demonstrated on 25μ diameter spots for typical polarization of 8μC/cm^2 [33] and switching voltages of 20 V across 4μ thick films, i.e., fields of 50 Kv/cm. Here the need of a photoconductor adds further leakage of charge and also limitation in cycle time to about 250μ sec.

The known magnetoferroelectrics should have polarizations comparable to other oxide ferroelectrics, i.e., 5-20μC/cm^2. $BiFeO_3$ itself has too high a coercive field for switching or even for measurement of hysteresis. The solid solutions such as $Bi_{.9}Nd_{.1}FeO_3$ may have lower coercivity, although this is not definitely known. It appears that the conductivity can be sufficiently low, $< 10^{-8}\Omega^{-1}cm^{-1}$. Nickel-iodine boracite switches with a field of 5 Kv/cm which is typically that of most usable ferroelectrics.

As noted in recent reviews,[30] ferroelectrics will not find wide-spread application in digital memory and display. The potential utilization of the ferroelectric property of magnetoferroelectrics is basically the same as for ferroelectrics not having magnetic ordering. The applications of interest depend upon their optical properties, i.e., the large changes in birefringence produced by switching the polarization. Possible applications are shutter array as a page composer in a holographic memory system and light valves in slow scan displays.

Optical Properties

Pertinent optical properties are absorption, linear birefringence, and Faraday rotation (magnetic circular birefringence). The absorption is most critical for transmitted signals. One can assume the linear birefringence change with polarization reversal in a magnetoferroelectric is of the order of 0.5 to 1 percent (i.e., 10^4 to 10^5 degrees/cm) as for good ferroelectrics. Then for rotations of 90° or 180° of transmitted light in the visible range, as desirable for phase shifters in optical processing,[30] one needs thicknesses of the order of 50 to 100μ. The absorption coefficient must be $\leq 10^2$ cm^{-1} to permit 10 to 50 percent transmission for these thicknesses. Many ferroelectric materials have much lower absorptions so that for half-wave retardation they are virtually lossless. There are insufficient absorption data on most magnetoferroelectrics. The boracites have strong absorption bands with coefficients from about 5×10^2 to 3×10^3 cm^{-1} [39] in the visible. Other materials also have 3d transition metal cations, such as Fe^{3+}, Ni^{2+}, Cr^{3+} and Mn^{3+} producing absorption bands in the visible. So one expects low transmission of visible and ultraviolet light with absorption coefficient or order 10^3 to 10^4 cm^{-1}. For instance the ferrimagnetic garnets have absorption values of $\sim 10^3$ cm^{-1}. Impurities and nonstoichiometry, particularly of oxygen, can increase the absorption of these oxidic materials. Thus it is questionable that the absorption coefficients of magnetoferroelectrics for the visible range would be decreased from $> 10^3$ cm^{-1} to $< 10^2$ cm^{-1} as would be desirable for use in place of good ferroelectrics alone. However it is likely that the magnetoferroelectrics containing transition metals may have much lower absorption coefficients in the near-to-medium infrared range as do the garnets and orthoferrites.

We must also note the distinction between uniaxial and biaxial crystals for use in optical processing. The uniaxial crystal with 180° domain switching, which is the most common, leaves transmitted light unaltered. The more useful effect requires a biaxial crystal where the optical index ellipsoid is rotated with polarization switching.[30] Of the known magnetoferroelectrics, we may cite $Bi_{.9}Nd_{.1}FeO_3$ as an example of a uniaxial and nickel-iodine boracite as a biaxial crystal.

The Faraday rotation F is the magnetooptical effect of major interest. For transmission application the parameter of concern is its ratio to absorption coefficient, F/α(deg) while for a magnetooptical memory it is $F^2/\alpha(deg^2/cm)$.[4] Rotations of $\pi/4$ radians are desired for transmitted signal processing (rotators, isolators, modulators, etc.) To attain this with acceptable loss an F/α parameter of 2.5 to 25 deg. is needed. For magnetooptic memories the F^2/α value should be $> 10^5$ and preferably $\approx 10^6$ deg^2/cm to be comparable to the intermetallic ferromagnets.

The pertinent data are not available for known magnetoferroelectrics. However estimates have been made on the basis of other known weak ferromagnets—orthoferrites, $FeBO_3$, FeF_3 —and the ferrimagnetic garnets. A reasonable estimate of the maximum likely spontaneous Faraday rotation is 10^3 deg/cm for which F/α is about 1 deg. For nickel-iodine boracite[34,36] at 0.633μ, F/α is around 4. The corresponding F^2/α value is 10^3 deg^2/cm assuming α is 10^3 cm^{-1}. As noted above, decreased absorption in the near-infrared could possibly increase the F/α parameter to the desirable range, assuming F did not change. Raising the F^2/α value to 10^5 deg^2/cm does not appear likely, however.

There is also a problem of interference of the linear birefringence with the Faraday rotation in magnetoferroelectrics. The interference depends upon the relative orientation of the magnetization, M, and polarization, P. Thus

for M⊥P the light propagating along the direction of M undergoes birefringent phase retardation. This results in an oscillating spatial variation of the plane of light polarization with period equal to the wavelength of the light and markedly reduces the maximum rotation. This is the case for naturally birefringment $FeBO_3$ and FeF_3 where rotations are limited to 0.7 and 0.3°.[35] According to the above estimates the linear birefringence is much greater than the Faraday rotation. Nickel-iodine boracite would be expected to show such interference since it has M⊥P. For M∥P one would have only the Faraday rotation for light transmitted along the magnetization direction. $Bi_{.9}Nd_{.1}FeO_3$ apparently satisfies this latter condition. Thus for utilization of the magnetooptical Faraday effect one would prefer a priori uniaxial crystals with M∥P. Favorable situations with M⊥P may occur, however. Miyashita and Murakami[36] found, for instance, that a 0.05 cm thick NIB platelet with light propagation in the (110) direction showed a good spontaneous rotation of 200-350 degrees/cm. They did not report the degree of ellipticity of the emerging light, though.

Magnetoelectric Coefficient

The linear magnetoelectric coefficient γ (actually the largest component of the linear magnetoelectric tensor) is the critical parameter for interaction of magnetic and electric fields in applications such as memories or control devices. The higher-order coefficients as well, however, enter into possible applications involving dynamic phenomena. A compilation[11] of measured coefficients gives a maximum of around 10^{-3} (c.g.s. units) with most antiferromagnets having values of order of 10^{-4} and ferrimagnets giving 10^{-5} to 10^{-6}. For a linear coefficient about 10^{-4} the estimated induced magnetization is 0.1 emu/cm^3 for an electric field of 5 Kv/cm and an induced polarization of 10^{-9} C/cm^2 for

a magnetic field of 10 kOe. This magnetization is comparable to that of very weak ferromagnets. Thus it is borderline for potential applications involving its use alone. The polarization is several orders of magnitude less than the spontaneous polarization of ferroelectrics. It is too low for use by itself.

The gyrator[37] can be taken as an example of the need for greater magnetoelectric coefficient for purely ME devices. For efficient use, the figure of merit $\alpha^2/\chi_e\chi_m$ should be ≈ 1 where χ_e and χ_m are normal electric and magnetic susceptibilities. The quantity $\alpha^2/\chi_e\chi_m$ for nickel-iodine boracite is about 5×10^{-3} which is very much less than required.

In addition to the magnetization and polarization we also need to consider the effects on the optical properties of the magnetoelectric interaction. These can be separated into static effects in magnetoferroelectrics and induced dynamic effects. The principal optical parameters are, as described above, absorption, rotation and linear birefringence. The magnetoferroelectrics can have domain switching by either applied magnetic or electric field. Again there are the two cases of $M \| P$ and $M \perp P$ to consider. In the first, switching of either magnetic or electric field can produce reversal of dielectric polarization and thus of linear birefringence for transverse light and reversal of Faraday rotation for transmission parallel to the unique axis. The second case involves a 90° change of magnetization direction with reversal of dielectric polarization and vice versa. Here one can still have reversal of the linear birefringence but the Faraday rotation will show interference with the linear birefringence. The relative magnitudes of the two optical effects, as discussed above, point toward utilization mainly of the linear birefringence. Other parameters are the electric or magnetic coercivities and domain size. The small magnetoelectric coefficients lead to only a small contribution to the fields which separately

are needed for domain switching of either the ferroelectric or weak ferromagnet These fields are of order 5 kV/cm or 5 kOe. The necessity of switching domains limits the minimum size of bits for memory applications to several microns in diameter.

The linear magnetoelectric effect in magnetoelectric materials causes plane-polarized light to become, in general, elliptically polarized, the orientation of the major axis depending on the path difference.[38,39] The linear ME effect also under certain conditions leads to irreversible light propagation; that is, light traveling in one direction in the material may move at a slightly different velocity from that traveling in the opposite direction. It can be shown that the change in index of refraction on reversing direction is given approximately by $|\Delta n| = 2|\alpha|$, or on the order of 10^{-3} [40] if we assume that the magnetoelectric coefficient is not much changed at optical frequencies from its low frequency value. While this is not a large index change, it should be easily measurable, and should lead to interesting interference phenomena between forward- and backward-traveling waves in materials where the absorption is not too high. It is possible that such interference effects might have useful applications, such as the precise control of electric or magnetic fields, or of temperature or pressure. It seems unlikely that this phenomenon can be achieved <u>any other way</u> than through the ME effect. The effect might be much larger at frequencies near resonances, where the effective permeability is large.[25]

The reflection of linearly polarized light from the surface of an ME results in rotation through an angle proportional to γ, thus of the order of minutes. The angle of inclination of the ellipse for transmitted light is also proportional to γ. So considerable increase of the linear magnetoelectric coefficient is needed for optical effects of this sort to be appreciable in comparison with ordinary magnetooptic and electrooptic effects.

The effects of higher-order magnetoelectric terms on the optical properties have been discussed by Ascher.[41] The interaction of a linearly polarized electromagnetic wave with a material of the proper magnetic structure through the quadratic magnetoelectric effect can yield second-harmonic generation and optical rectification. The effect again is proportional to the magnitude of the quadratic magnetoelectric coefficients. Too little is known about the magnitudes of these higher order terms to justify further speculation.

Collective Magnetic Resonances

Known magnetoferroelectrics are antiferromagnets with some exhibiting weak ferromagnetism. Therefore they have natural resonance frequencies falling in the millimeter and submillimeter wavelength range.[42] Neglecting losses, the resonance frequencies, ω, for uniaxial two-sublattice antiferromagnets are

$$\omega\pm/\gamma = [2\lambda K + (\beta H/2)^2]^{1/2} \pm H(1 - \beta/2)$$

where γ is the gyromagnetic factor, λ is the molecular-field exchange constant, K is the anisotropy constant, and β is the susceptibility ratio $\chi_{\parallel}/\chi_{\perp}$. For λK we may write $H_e H_a$ where H_e is the exchange field, λM, and H_a is the anisotropy field, K/M. M is the sublattice magnetization and H_a is assumed $\ll H_e$. Or the term $2\lambda K$ can be taken as the square of the "critical" field H_c which can range from 60 kOe to > 100 kOe. One must operate at applied fields, H, less than H_c to avoid "spin flop" to the state with the M's perpendicular to the applied field. Either resonance mode can be used in devices. The resonance linewidth ΔH can vary in a given material, depending on its purity, from hundreds to thousands of oersteds. The figures of merit are $F = (4H/\Delta H)^2$ for waveguide resonance isolators and $F = 4H/\Delta H$ for phase shifters.[43] Therefore the pertinent parameters are the critical field H_c and linewidth ΔH. For antiferromagnetic ferroelectrics such as $BiFeO_3$ or $YbMnO_3$, the critical field H_c is

expected to be about 100 kOe. Assuming a linewidth of 1 kOe or more, we find the applied fields would need to be of magnitude 5 to 50 kOe for reasonable figures of merit.

An applied electric field can affect the antiferromagnetic resonances through the magnetoelectric coupling. In a strongly anisotropic uniaxial antiferromagnet, magnetoelectric coupling can modify the zero-field resonance frequency[44] to

$$\omega_o/\gamma = H_c \pm H_{me}$$

where $H_{me} = \alpha E$, α is the magnetoelectric effect coefficient, and E is the applied electric field. For an α of 10^{-4} - 10^{-3}, E would need to be very high, $\sim 10^8$ V/cm, to be an appreciable fraction of H_c. Shavrov[44] suggested that a smaller electric field could produce a significant resonance shift in those antiferromagnets showing the magnetoelectric effect in which the minimum excitation energy results from magnetostriction effects only. This should be an observable effect; the resonance, however, will lie in the low microwave region, which does not seem to be of great interest at present. No experimental studies have been made.

For ferroelectric antiferromagnets, an oscillating electric field is equivalent to an added component to the applied magnetic field given by[45]

$$H \rightarrow H + 2\,\xi M$$

where $\xi = \dfrac{\gamma \eta^2 M (E(\omega_e))^2 \varphi}{8 \omega_e}$, where ω_e is frequency of the electric field and φ is a polarization factor which may be as large as unity.

η is the magnetoelectric coefficient if the effect is expressed in terms of cross product of the sublattice magnetizations. According to Akhiezer,[45] η is $\sim 10^{-3}$. Here the contribution depends on the term $(\eta M)^2$, and may become appreciable for strong sublattice magnetizations, that is, for $\eta M \sim 10$ or more. Also it should

be remembered that the magnetoelectric coefficient depends on frequency and may show resonant behavior at antiferromagnetic resonance frequencies.[46] Unfortunately, no experimental investigations of these effects have been attempted.

Next, we turn to ferromagnetic (or more properly ferrimagnetic) resonance in weak ferromagnets and conventional ferrimagnets. For the low-frequency mode for which the net magnetic moment vectors of each magnetic unit cell remain parallel to each other and to the applied field, it is adequate to describe the system as if it were a simple ferromagnet characterized by a magnetization and spin that are just the vector sums of those due to the individual sublattices.[42]

Ferromagnetic resonance has been observed in rather few weak ferromagnets. This is because good single crystals are required for its observation. This is in contrast to the situation in conventional ferrimagnets, where FMR is observed, and used, in polycrystals and sintered materials. The reason for this is just that, in a polycrystalline weak ferromagnet, the distribution of magnetization directions from crystallite to crystallite produces a wide range of effective resonance fields, and thus an extremely broad line. In a garnet, say, with its considerably larger total magnetization, the interaction of the magnetizations of adjoining crystallites tends to produce a more uniform magnetization, and thus a much narrower line.[47] To our knowledge, FMR has not been observed in any weak ferromagnets in which linear magnetoelectric coefficients have been measured or in which ferroelectricity has been demonstrated; it has, however, been observed in a number of rather similar materials, and its detection in ME weak ferromagnets presumably awaits only the preparation of single crystals. Since the total magnetization is small, the location of the resonance is determined almost entirely by anisotropy properties, the specimen shape making little difference. The resonance frequency, for not too small applied fields,

and for crystals of not too low symmetry, is given approximately by[48]

$$(\omega/\gamma)^2 = (H + C_1 H_a)(H + C_2 H_a), \quad -1 \leq C_1, C_2 \leq 1$$

where the C's are factors depending on the crystal orientation and type of anisotropy. (For a uniaxial crystal magnetized along the axis, $C_1 = C_2 = 1$, for instance.) Thus depending on these factors and the magnetization, the resonance may be found anywhere from very low microwave to near millimeter-wave frequencies in reasonable applied fields.

Among conventional ferrimagnets, the only ones known to display linear ME effects are the gallium ferrites. Some unusual and somewhat controversial electric-field effects on ferromagnetic resonance lines have been observed in these materials.[49,50] These effects are by no means small, and do not seem to be attributable directly to effects of the magnetoelectric interaction. This is discussed further in Table III. Resonance linewidths are 400 Oe or more.

Improvements in material purity, stoichiometry, and so forth, leading to improved linewidths are important not only for microwave, but also for optical, applications. For high-speed optical modulation, rf losses must be low.[51] The FMR linewidth, proportional to the magnetic damping, provides a good measure of this. Known ME's have a long way to go to catch up with YIG (linewidth as narrow as 0.5 Oe) in magnetic switching speed.

Conclusions and Recommendations

From the foregoing discussion and from Table III, it appears that there are four applications areas for ME materials which, on paper, are decidedly promising and merit further investigation. These are:

(1) Magnetic field switching or modulation of electric polarization, in turn affecting electrooptic properties,

avoiding the need for thin plates and high applied electric fields (the magnetic fields required are moderate—a few kOe at most).

(2) Exploitation of high dielectric constant in high-frequency, low-loss microwave Faraday rotators.

(3) Efficient generation and/or modulation or modification of spin waves or hybrid spin-electromagnetic waves utilizing the magnetoelectric effect.

(4) Use of the phenomenon of irreversible light propagation in one or another type of highly sensitive interference sensors.

Some other reasonably good possibilities are given in Table III. There does not seem at present to be any device need which can be filled uniquely or most effectively by devices utilizing the particular properties of known ME's. This may change as systems operating in millimeter-wave and infrared regions become more common and as some prototype ME devices are demonstrated. Incidentally, several of the devices described in Table III require good-sized (1 - 15 kOe) static magnetic fields for their operation. High fields (over small regions) are particularly necessary for millimeter-wave devices. A natural application of rare-earth-cobalt permanent magnets is for the production of such fields.

Each of the suggested uses above has both advantages and disadvantages or impediments. The descriptions above point out the obvious advantages; the drawbacks are summarized very briefly here. For magnetic-field control of electrooptic properties, the chief possible disadvantages are high absorption, nullifying the advantage of thicker samples, and effects of natural and magnetic birefringence. The first difficulty may not be too severe in good crystals in

some region in the near infrared, and the second can be to some extent designed around.[35] For efficient high-frequency Faraday rotators or phase shifters, the principal difficulties are that there are insufficient experimental data to establish clearly the superiority of any particular magnetoferroelectric (compared to some non-ferroelectric material, such as iron borate,[52] for example) and that there is still some controversy over the properties of the highest-dielectric-constant materials (see Table II). As for the last two proposed applications, the overwhelming drawback is that the phenomena involved have never been observed experimentally. (To our knowledge, no attempts to observe them have been made.) Until this is done, detailed discussion of applications appears to us otiose.

If the unique properties of ME materials are to be exploited in devices, we believe the following should be done, at a minimum:

(1) Further experimental work should be done on some of the better-known ME materials, so that reasonably complete and reliable sets of data are available for at least a few materials. Some work towards better crystals should be included, aiming particularly at higher transparency, lower conductivity, narrower resonance lines.

(2) Further studies should be conducted of antiferromagnetic ferroelectrics (such as $BiFeO_3$ and hexagonal rare-earth manganites), which are probably just as useful as weakly ferromagnetic ferroelectrics for many millimeter-wave and far-infrared applications. Work on crystal growth and electrical properties is of primary importance.

(3) Lingering questions concerning properties of lead-based materials should be answered by applying modern materials characterization techniques to samples of these materials.

(4) Attempts should be made to demonstrate magnetoelectric coupling of spin waves to external electric fields, to demonstrate irreversible light propagation, and to measure the components of the magnetoelectric tensor at microwave and higher frequencies. Further theoretical work along these lines is also desirable.

(5) The search for improved materials should continue, although it seems to us that dramatic improvements should not be counted on, and expectable improvements within classes of materials already studied are more likely to lead to early application.

These recommendations are not to be considered as fixed; they are intended in part to stimulate discussion among all those with a present interest in magnetoelectric materials. In addition, those involved in such work ought to maintain a broad interest in all aspects of the development of the as yet little utilized regions of the electromagnetic spectrum.

Proposed Applications of ME Materials

Device	Frequency Range*	Functions	Phenomenon Used**	Comments	References
1) Magnetoelectric gyrator	AF-RF	isolation, phase-shifting, amplification	c	Requires large ME susceptibility, impractical (see p. 21)	25,37,53
2) Magnetoelectric memory	---	bit-by-bit read write memory	c	Requires both E and H field to switch magnetoelectric domain, thus writing more similar to coincidence writing in ferrite cores than proposed optical-read memories; writing speed possibly slow unless very high fields used; reading by sensing of magnetization change resulting from ac electric field may be very fast. Overall present prospects definitely unpromising.[55] Bit density fairly low.	11,25,54 55
3) Optical-rectification IR detector	FIR, SMM probably	sensitive broad-band detector in difficult region	e	The terms $\frac{1}{2}\alpha_{ijk}H_iE_jE_k$ and $\frac{1}{2}\beta_{ijk}E_iH_jH_k$ in the free energy (Table I) lead to changes in polarization and magnetization, respectively, (the inverse magnetoelectric Pockels and "Mockels" effects) when an electromagnetic wave passes through the material. The conventional wisdom that higher-order optical-property coefficients are frequently less frequency-dependent than linear ones leads one to conjecture that such devices might be useful in the FIR or SMM region. Components of the α and β tensors have been measured in a few materials, but neither of these specific inverse, rectification effects has been demonstrated experimentally.	56
4) Electric-field-controlled ferromagnetic resonance device	MW, possibly MM	switch or isolator, most likely—possibly temperature-stabilized (by E field) FMR device	c?	Rather large changes in the K-band ferrimagnetic resonance spectrum of $Ga_{.85}Fe_{.15}O_3$ were found by Petrov and coworkers[49] on application of 2-3 kV/cm electric fields. A shift of line position and a reduction of linewidth of kOe magnitude and a simplification of line shape were observed. Folen and Rado[50] pointed out that the observed effects were too large to be directly attributable to the magnetoelectric effect, and suggested that they might be due to heating of the samples by the applied E field, producing changes in the anisotropy energy. Experimental work of Folen and Rado under slightly different conditions also did not show any large effects. While this seems to be the most likely explanation, there is perhaps room for further experimental work, since there might be an increase in the effective magnetoelectric effect near the resonance,[25] and since the unusual line shapes are not really accounted for. For a material with a tolerably narrow resonance line, which also has a reasonably low dc electrical conductivity to minimize Joule heating effects, it should be possible to use an applied E field to offset the drift in the resonance caused by temperature change due to microwave absorption. This would greatly simplify the circuitry for the applied variable H field being used for phase shifting. The present prospects for this are not good, though, since a satisfactory material is not known. Good single crystals are required.	49,50

Device	Range*	Functions	Used		References
5) Electric-field-controlled antiferromagnetic resonance device	MM, SMM, MW?	switch, isolator, phase shifter	c	Does not seem promising at present. (See discussion, p. 24) Almost no experimental work has been done.	42-44,23
6) Magnetically switched electrooptic device	V, IR	optical switch, isolator, amplitude modulator	b	To obtain an electrooptic shutter operating by ferroelectric domain reversal (using the Pockels effect) it is necessary to apply high electric fields to the sample, thus usually requiring the use of their samples and either transparent electrodes or overlying fine wire grids. In certain magnetoferroelectrics, the spontaneous polarization can be reversed by applying a magnetic field (see pp. 10,22) of not more than a few kOe. This eliminates the need for thin plates (if absorption not too high) and high electric fields, which could be troublesome in certain environments. Something is presumably sacrificed in frequency response. A modulator working along the same lines would probably work best if it involved a change in domain pattern, rather than relying on the magnetoelectric effect. The kind of coupling required has been demonstrated in the boracites.[12] For the present application, uniaxial materials might be somewhat simpler to work with. Any device of this sort of course has to prove its superiority to straightforward magnetooptical devices operating at the same frequency.	
7) Improved microwave phase shifter or polarization rotator	MW, MM?	phase shifter, Faraday rotation	d	At frequencies well above the ferromagnetic resonance frequency, the figure of merit for a microwave Faraday rotator is proportional $\epsilon' M_z/\epsilon''$, where M_z is the magnetization component in the direction of propagation and ϵ' and ϵ'' are the real and imaginary parts of the dielectric constant at the frequency of operation. Even at microwave frequencies, the dielectric constant in lead-based ME's may be 2 or more orders of magnitude greater than in comparable conventional ferrites. So the lower magnetization in weak ferromagnets may not be too severe a problem. Additional study of the lead-based materials would be a good idea (see Table II). Also possibly worth consideration are frankly two-phase ferroelectric ferromagnetic materials being developed in Poland for this type of application.[58] No similar advantage is found for isolators.	57,3,58
8) Multiple-state memory element	---	element for non-binary memory	a	It has been frequently suggested that the presence of more than 2 discernible polarization states in ME materials could be used for storing more than one bit of information in a single domain. But the packing density still would not be very high, and the associated electronics rather complicated, and the advantages nebulous at best so such devices do not seem promising.	
9) Electric-field-modulated visible Faraday rotator	V, IR	amplitude modulator	a	Suppose a polarizer, Faraday rotator, and analyzer are set so that no light is transmitted. An electric field applied to the rotator will cause the light being transmitted to become elliptically polarized leading to a transmitted signal whose strength depends on the applied electric field. This will occur in any material, but probably most strongly in one which is ferroelectric. But there does not seem to be any particular advantage to this over any of the many other methods of accomplishing the same result. If any ME material were known with stripe domains, an electric-field modulated stripe-domain deflector[59] might be an interesting thing to try.	

Device	Frequency Range*	Functions	omenon Used	Comments	Reference
10) Magnetically (electrically)-modulated piezoelectricity (piezomagnetism) device	AF, RF	variable transducer	e	The coefficients s' and s'' (Table I) lead to electric and magnetic field modifications, respectively, of the effective elastic moduli, which might be used to vary the frequency of a transducer somewhat. To our knowledge, no experimental work has been done.	60
11) Irreversible-light-propagation device	V, IR	sensor, optical isolator?	c	As described on p. 23, under some circumstances, the velocity of light propagation in ME materials is indicated by theory to depend on the direction of transmission (i.e., "forward" and "backward" are not the same). The corresponding effective change in index of refraction is about 10^{-3}. While this is not a large change, observable interference effects should occur when forward and backward beams are combined. Other electro- and magnetooptical effects occurring simultaneously might obscure these effects without proper experimental arrangement, including applied fields. The interference pattern should be very sensitive to applied field changes and thus might serve as a sensor. In very transparent materials, this effect might be used for optical isolation, or (with applied field tuning) beam deflection. It is very unfortunate that no observation of this effect has been made.	25,38,46
12) Magnetoelectric non-linear-optical device	V, IR, SMM	frequency doubler, parametric oscillator	e	The non-linear terms responsible for rectification (item 3) could also be used, in conjunction with the usual non-linear susceptibility to produce second-harmonic generators or optical parametric oscillators which could be controlled by applied fields. For doubling the antiferromagnetic resonance frequency, the magnetoelectric non-linear effects could outweigh the usual ones. One might also hope that precise temperature control of OPO's, now necessitating voluminous and complex ancillary equipment, could be replaced by control with a moderate electric field. Again, the basic effects (that is, properties of the relevant tensors in the visible-ir range) have not been observed, and device design is complicated by the variety of effects all occurring at once.	11,56
13) Magnetoferroelectric semiconductor spin-wave generator	---	generate spin waves	c	Akhiezer[61] suggests that in an antiferromagnetic ferroelectric semiconductor, it should be easier to generate a spin wave than in an ordinary magnetic semiconductor, because of the direct coupling between the electric field and the spins; furthermore spin waves should be generated by a strong enough applied dc electric field much in the way ultrasonic waves are amplified in piezoelectric semiconductors. No experiments have been attempted.	61
14) Oscillating-electric-field magnetoelectric spin-wave amplifier	---	amplify spin waves	c	A high-frequency electric field acting on an antiferromagnetic ME material should also lead to spin wave amplification through the effective change in magnetic field discussed on p. 25. A strong applied uniform magnetic field and a good-sized sublattice magnetization are also necessary. No experiments reported.	45
15) Coupled-wave devices	---	produce new types of hybrid waves	c	In analogy with conversion of spin waves to magnetoelastic waves through magnon-phonon coupling, a number of suggestions have appeared in the Russian literature concerning the production of novel hybrid spin-electromagnetic or spin-acoustic waves through the magnetoelectric effect. The possible uses of these hybrid excitations do not seem to have been considered, though.	62

* Of the detected electromagnetic field-not of modulating fields or of other types of waves.
Notation: AF - audio frequency, RF - radio frequency, MW - microwave region, MM - millimeter wave region, SMM - sub-millimeter wave on very-far-infrared region (0.1-1 mm wavelength), FIR - far infrared (20-100μ), IR - infrared (0.8-20μ), V - visible.

** See page 8.

References

1. V. E. Wood et al, Annual Technical Report to ARPA on Contract DAAH01-70-C-1076, June 30, 1971 (AD 726201).
2. R. R. Birss, Symmetry and Magnetism (North-Holland, Amsterdam, 1966).
3. B. Lax, Proc. IRE 44, 1368 (1956).
4. R. Cohen and R. S. Mezrich, RCA Review 33, 55 (1972).
5. H. Schmid, Réunion Française de Ferro-electricité, Orléans, (1972); G. T. Rado and V. J. Folen, J. Appl. Phys. 33, 1126 (1962).
6. J. Kobayashi et al, J. Phys. Soc. Japan 28 Suppl., 67 (1970).
7. C. Haas, IEEE Trans. Mag. 5, 487 (1969).
8. E. V. Chenskii, Sov. Phys.-Solid State 11, 534 (1969); M. S. Shur, Bull. Acad. Sci. USSR, Phys. Ser. 33, 187 (1969).
9. P. J. Freud, Phys. Rev. Letters 29, 1156 (1972); I. G. Austin and R. Gamble, "Eilat Conference on Conduction in Low-Mobility Materials", (Taylor and Francis, London, 1971), p. 1.
10. R. M. Hornreich, Solid State Communs. 7, 1081 (1969).
11. E. F. Bertaut and M. Mercier, Mat. Res. Bull. 6, 907 (1971).
12. E. Ascher, H. Rieder, H. Schmid and H. Stossel, J. Appl. Phys. 37, 1404 (1966); H. Schmid, Rost Kristallov 7, 32 (1967) (translation: Growth of Crystals 7, 25 (1969) Consultant's Bureau, New York).
13. J. M. Moreau, C. Michel, R. Gerson, and W. J. James, J. Phys. Chem. Solids 32, 1315 (1971); J. R. Teague, R. Gerson, and W. J. James, Solid State Communs. 8, 2073 (1970).
14. V. M. Yudin, Sov. Phys.-Solid State 8, 217 (1966).
15. V. E. Wood and A. E. Austin, Proc. 18th Annual Conference on Magnetism and Magnetic Materials (AIP Conference Proceedings, to be published 1973).
16. I. H. Ismailzade, R. G. Yakupov, and T. A. Melik-Shanazarova, Phys. Stat. Sol. (A) 6, K 85 (1971).
17. G. A. Smolenskii et al, Ferroelectrics and Antiferroelectrics (Izdatelstvo "Nauk", Leningrad, 1971) (translation: U. S. Army Foreign Science and Technology Center, 1972, AD 741037); Chap. 18.
18. S. Nomura, H. Takabayashi, and T. Nakagawa, Japan J. Appl. Phys. 7, 600 (1968).
19. D. N. Astrov et al, Sov. Phys.-JETP 28, 1123 (1969).

20. M. Eibschutz and H. J. Guggenheim, Solid State Communs. 6, 737 (1968); M. Eibschutz et al, Physics Letters 29A, 409 (1969); D. E. Cox et al, J. Appl. Phys. 41, 943 (1970).
21. B. I. Al'shin et al, Sov. Phys.-JETP Letters 12, 142 (1971).
22. E. F. Bertaut, F. Forrat, and P. Fang, Comptes Rendus 256, 1958 (1963); V. A. Bokov et al, Soviet Phys.-Solid State 5, 2646 (1964); H. Tamura et al, Japan J. Appl. Phys. 4, 621 (1965); R. Pauthenet and C. Veyret, J. de. Phys. 31, 65 (1970).
23. T. Penney, P. Berger, and K. Kritiyakirana, J. Appl. Phys. 40, 1234 (1969); K. Kritayakirana, P. Berger, and R. V. Jones, Optics Communs. 1, 95 (1969).
24. M. Mercier, P. Bauer, and B. Fouilleux, Comptes Rendus 267B, 1345 (1968).
25. T. H. O'Dell, The Electrodynamics of Magneto-Electric Media (North-Holland Amsterdam, 1970), and references therein.
26. S. Shtrikman and D. Treves, Phys. Rev. 130, 986 (1963); R. M. Hornreich, J. Appl. Phys. 41, 950 (1970).
27. G. T. Rado, J. Appl. Phys. 37, 1403 (1966).
28. G. R. Lee, Phil. Mag. 18, 1315 (1968).
29. A. H. Eschenfelder, J. Appl. Phys. 41, 1372 (1970); E. W. Pugh, Proc. 17th Annual Conference on Magnetism and Magnetic Materials (AIP Conf. Proc. #5, 1972).
30. L. K. Anderson, Ferroelectrics 3, 69 (1972).
31. W. Strauss, J. Appl. Phys. 42, 1251 (1971).
32. M. H. Francombe, Ferroelectrics 3, 199 (1972).
33. R. R. Mehta, J. Appl. Phys. 42, 1842 (1971).
34. R. V. Pisarev, S. D. Prokhorova, and G. T. Andreeva, Soviet Phys.-Solid State 11, 766 (1969).
35. R. Wolfe, A. J. Kurtzig, and R. C. LeCraw, J. Appl. Phys. 41, 1218 (1970).
36. T. Miyashita and T. Murakami, J. Phys. Soc. Japan 29, 1092 (1970).
37. B. D. H. Tellegen, Philips Research Reports 3, 81 (1948).
38. R. R. Birss and R. G. Shrubsall, Phil. Mag. 15, 687 (1967).
39. V. M. Lyubimov, Sov. Phys.-Crystallog. 13, 739 (1969).
40. V. M. Lyubimov, Sov. Phys.-Crystallog. 13, 877 (1969).
41. E. Ascher, Phil. Mag. 17, 149 (1968).
42. S. Foner, Chap. 9 in Magnetism, Vol. 1 (G. F. Rado and H. Suhl, eds.) (Academic Press, New York 1963).

43. G. S. Heller, J. J. Stickler, and J. B. Thaxter, J. Appl. Phys. 32, 3075 (1961).

44. V. G. Shavrov, Sov. Phys.-Solid State 7, 265 (1965).

45. I. A. Akhiezer, and L. N. Davydov, Sov. Phys.-Solid State 13, 1499 (1971).

46. R. A. Fuchs, Phil. Mag. 11, 647 (1965).

47. A. M. Clogston, J. Appl. Phys. 29, 334 (1958).

48. C. Kittel, Phys. Rev. 73, 155 (1948).

49. M. P. Petrov, S. A. Kizhaev, and G. A. Smolenskii, Phys. Stat. Sol. 30, 871 (1968); JETP Letters 6, 306 (1967).

50. V. J. Folen and G. Rado, Solid State Communs. 7, 433 (1969); J. Dweck, Phys. Rev. 168, 602 (1968).

51. R. C. LeCraw, Intermag Conference presentation, Stuttgart, 1966 (unpublished).

52. R. C. LeCraw, R. Wolfe, and J. W. Nielsen, Appl. Phys. Letters 14, 352 (1969).

53. J. W. Miles, J. Acoust. Soc. Amer. 19, 910 (1947).

54. T. J. Martin, Phys. Letters 17, 83 (1965).

55. T. H. O'Dell (private communications).

56. E. Ascher, Helv. Phys. Acta 39, 446 (1966); L. N. Bulaevskii and V. M. Fain, JETP Letters 8, 165 (1969).

57. C. L. Hogan, Bell Syst. Tech. J. 31, 1 (1952).

58. K. Leibler, V. A. Isupov, and H. Bielska-Landowska, Acta Phys. Polon. A40, 815 (1971).

59. D. S. Lo, D. I. Norman and E. J. Torok, J. Appl. Phys. 41, 1342 (1970); T. R. Johansen, D. I. Norman and E. J. Torok, J. Appl. Phys. 42, 1715 (1971).

60. E. Ascher and H. Schmid (private communication).

61. A. I. Akhiezer and I. A. Akhiezer, Sov. Phys.-JETP 32, 549 (1971).

62. A. I. Akhiezer and L. N. Davydov, Soviet Phys.-Solid State 12, 2563 (1971); V. G. Baryakhtar and I. E. Chupis, Sov. Phys.-Solid State 10, 2818 (1969), 11, 2628 (1970); I. F. Ioffe and A. L. Kazakov, Sov. Phys.-Solid State 13, 1806 (1972).